Our Ref. No.: 005513.P018

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application for:)	
)	Examiner: Le, Thao X.
Michael C. Green et al.)	
)	Art Unit: 2814
Serial No. 10/665,298)	
)	
Filed: September 17, 2003)	
)	
For: **REDUCING DARK CURRENT OF**)	
PHOTOCONDUCTOR USING HETEROJUNCTION)	
THAT MAINTAINS HIGH X-RAY SENSITIVITY)	

DECLARATION PURSUANT TO 37 C.F.R. §1.132

Mail Stop Amendment
Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450

Dear Sir/Madame:

I, Michael C. Green, hereby declare that:

1.   I am a citizen of the United Kingdom.

2.   I currently reside at 4055 Manzana Lane, Palo Alto, CA 94036.

3.   I am currently an employee at Varian Medical Systems, Inc. ("VMS") in Mountain View, CA.

4.   I have been employed by VMS from 2001 to Present.

5.   My current title at VMS, Inc. is Senior Scientist.

6.   I am a co-inventor of the above-identified patent application.

7.   Varian Medical Systems Technologies, Inc. ("VMST") is the assignee of the above-identified patent application. VMST is a wholly owned subsidiary of VMS.

8.   The Examiner has cited parts of U.S. Patent No. 6,403,905 issued to Ikeda et al. ("Ikeda") filed March 23, 2000 issued June 11, 2002 against the claims (pending claims 1-29 and 32-37 attached hereto) of the above-identified application. I have reviewed relevant parts of Ikeda, and the claims of the above-identified application, which require a first and second semiconductor material be halides. <u>I provide the following expert opinion regarding halogen-doped amorphous selenium, the definition of a halide semiconductor, and mercuric iodide.</u>

9.   Ikeda, column 7 lines 20-23 states "Furthermore the n-type Se film 211 is formed so as to have a low resistivity by adding a large amount of a halogen such as Cl or I to Se to produce a large number of free electrons".

10.   Doping of a semiconductor film such as Se is done to alter resistivity, typically to reduce resistivity by increasing the number of mobile holes and/or electrons. For the amorphous selenium film of Ikeda, the effect of the halogen atoms incorporated into the selenium lattice as dopants is to increase the mobility of electrons and holes in the amorphous selenium semiconductor. This lowers the resistivity of the amorphous selenium substantially. When dealing with semiconductor dopants the difference between a "small amount" of a dopant element and a "large amount" of a dopant element present in a semiconductor material might be the difference between dopant concentrations of 1 part per million (ppm) and 100 ppm.

11.   There is an optimum concentration of Cl or I that will effectively compensate defects in the amorphous selenium and maximize the conductivity. This optimum is typically at a level of less than 100 ppm of Cl or I in the amorphous selenium lattice. (see "Effect of combinational doping on x-ray sensitivity of a-Se films." Suresh Chand 1998 *J. Phys. D: Appl. Phys.* 31 1049-1051) Too much dopant will degrade the performance of the material. The phrase "a large amount of halogen" in Ikeda implies perhaps 50 ppm of Cl or I.

12.   A halide compound has a particular stoichiometry. For example selenium forms two selenium halides when it reacts with the halogen chlorine. These are Se_2Cl_2

and $SeCl_4$. They are covalent molecular compounds with fixed selenium to chlorine atomic ratios of 1:1 and 1:4 respectively. That is, the foregoing halide compounds contain a concentration of 500,000 ppm and 800,000 ppm iodine, respectively. Moreover, a covalent compound has a specific molecular structure. Such a compound has its own unique physical properties that usually differ greatly from those of the constituent elements. Se_2Cl_2 is an oily, pungent-smelling, liquid that freezes at -85 deg C. $SeCl_4$ is a pale yellow, volatile, hygroscopic solid that is readily hydrolyzed by water. Neither of the selenium halides Se_2Cl_2 or $SeCl_4$ is present in an amorphous selenium semiconductor that has been doped with a low level of chlorine, and due at least to their physical structure, neither is desired. Rather, for selenium doped with chlorine, the chlorine is present as an interstitial impurity that acts like a semiconductor dopant and modifies the internal electronic energy levels, compensating for deep level photostructural defects that can act as traps, thereby increasing the mobility of electrons and holes in the amorphous selenium. (see "Effect of chlorine doping on photostructural defect states in amorphous selenium films." Chand, S; Sharma, G. D.; Bhatheja, R. C.; Chandra, S: Applied Physics Letters, Volume 59, Issue 27, December 30, 1991, pp.3514-3515) Selenium bromides Se_2Br_2 and $SeBr_4$ exist, and are the analogs of the chlorides Se_2Cl_2 and $SeCl_4$ (e.g., as physical structure analogs). (see "Comprehensive Inorganic Chemistry" edited by J.C. Bailar et al., volume 2, pages 955-961.) However, the analogous selenium halides with iodine are not known. Therefore the formation of the compound selenium iodide is not even a chemical possibility.

13. While the compounds Se_2Cl_2 $SeCl_4$, Se_2Br_2 and $SeBr_4$ exist, as described in paragraph 12, above, and are halide compounds, they are not semiconductors. In the case of these selenium halide compounds the constituent atoms of the compounds are too electronegative to result in the formation of a semiconducting compound. Semiconduction naturally occurs at the boundary between metals and insulators. For pure elements this occurs at Group IVA of the periodic table of elements, that contains silicon and germanium. Elements to the left of Group IVA are increasingly

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electropositive and metallic in character; elements to the right of Group IVA are increasingly electronegative and insulating. Semiconducting compounds can be formed by a combination of an electropositive element and an electronegative element, symmetrically placed to the left and to the right of Group IVA in the periodic table. Thus the semiconductor GaAs is formed from gallium an electropositive element in Group III and arsenic an electronegative element in Group V. The critical factor is that Ga and As are symmetrically placed in the periodic table on either side of the semiconducting element germanium. In the compound GaAs the electronegativities of the two constituent elements and their electronic structures balance out to result in a semiconductor. Other III-V semiconductor compounds like InSb and InP exist and are widely used in devices. Selenium can form semiconducting compounds. However, selenium is an electronegative element in Group VI, so, to balance its electronegativity and electronic structure, it should be combined with an electropositive element in Group II of the periodic table, thus forming a II-VI semiconductor. (Group IIB and Group VIA elements are symmetrically placed about the semiconducting elements of Group IVA). Compounds of selenium that are II-VI semiconductors, such as CdSe, do exist and are commercially important. However, halogens are more electronegative than selenium, which is already an electronegative element, so halogens do not have the required charge-balancing electropositive properties to be able to form selenium halides that are themselves semiconductors.

14.   Amorphous selenium is a semiconductor and is a black solid, (red when finely powdered), having the lattice structure of a glass. This physical structure and the chemical identity of amorphous selenium is retained in amorphous selenium semiconductor films when they are doped with chlorine or iodine. Selenium doped with Cl or I is not a halide semiconductor.

15.   Mercuric iodide is a halide semiconductor. It is a covalent chemical compound, which has precisely two atoms of iodine chemically combined with each atom of mercury. It is one of a family of mercury halides which have the formula Hg_2X_2

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or HgX_2 where X= F, Cl, Br or I. Mercuric iodide, HgI_2, is a wide band-gap semiconductor. It is a halide compound containing more than 66 At. % of halogen. It has a specific crystalline structure, resulting from the directional covalent bonds between the mercury and iodine atoms, that is uniquely characteristic of the material. **Figure 1** shows the crystalline structure of alpha mercuric iodide. This crystal structure is intimately involved with the electron and hole transport properties of the halide semiconductor.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-identified application or any patent issued thereon.

Respectfully submitted,

Dated: __Nov. 6th__, 2006

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2.5. HALIDES

Introduction

The only known halides analogous to the sulphur compounds S_2A_2 are the selenium chloride and bromide and the tellurium iodide. The simple selenium dihalides have not been isolated in the solid state, but may be present in the vapour of the tetrahalides, whereas tellurium dichloride and dibromide can be isolated as solids, although they disproportionate rather readily to the metal and the tetrahalide; the polonium dihalides are more stable in this respect. The thermodynamic stability of the tetrahalides increases in passing from selenium to tellurium and in the highest oxidation state the only hexahalides known are the fluorides. These are, as one would expect, the most volatile of all the halides and are predominantly covalent in character, since the central atom could not possibly have as high a charge as $+6$.

Monohalides, X_2A_2

Fluorides of this composition are unknown, but selenium monochloride and monobromide are well established and are very similar in chemical properties to their sulphur analogues. Both compounds are oily, pungent smelling liquids which decompose at their boiling points (Table 7) to selenium and the tetrahalide

$$2Se_2A_2 = SeA_4 + 3Se$$
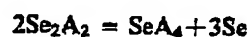
but some selenium dihalide may be present in the vapour of the decomposing monohalides.

The two monohalides are made by reaction of the stoichiometric quantities of the elements or, better, by adding the halogen to a suspension of selenium in carbon disulphide

TABLE 7. PROPERTIES OF THE MONOHALIDES, Se_2A_2

	Se_2Cl_2	Se_2Br_2
Colour	Brownish-red	Blood red
Melting point, °C	-85	—
Boiling point, °C	127/733 mm (d)	225–230 (d)
ΔH vap., kcal/mole	18[a]	—
Conductivity, mhos/cm	$2 \times 10^{-7}(18°)$	—
Density, g/cc	2·7741 (25°)	3·604 (15°)
Heat of formation		
ΔH_f, 298, kcal/mole	$-22·2$[a]	—
Free energy of formation		
ΔF_f, 298, kcal/mole	$-18·2$[a]	—

[a] A. Glassner, U.S.A.E.C. Report ANL-5750 (1958).   d = decomposition.

until dissolution of the element is complete and precipitation of the tetrahalide begins[81]. They can also be made by reducing the tetrahalide with selenium at 120° in a sealed tube and by reaction of selenium, some non-metal selenides or selenium dioxide with a variety of non-metal chlorides or bromides. The compounds are purified either by distillation under reduced pressure in the presence of elementary selenium or by precipitating them

[81] H. Stammreich and R. Forneris, *Spectrochim. Acta*, 8 (1956) 46.

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selenium with lithium or magnesium hydroxides[75] and the telluride by electrolysis of sulphuric acid (15–50%) with a tellurium cathode[18]. Hydrogen diselenide is thought to be formed when selenous acid is reduced with aluminium in hydrochloric acid[76], but little is known about this compound.

Evidence for the existence of hydrogen polonide is somewhat scanty; it seems only to have been prepared on the trace ($\sim 10^{-10}$ g) scale by reduction of polonium in acid solution

TABLE 6. SOME PHYSICAL PROPERTIES[a] OF H_2Se, H_2Te AND H_2Po

	H_2Se	H_2Te	H_2Po
Melting point, °C	−65.73°	−51°	−36°(?)
ΔH fusion, kcal/mole	0.6011	0.970	—
Boiling point/760 mm, °C	−41.3°	−4°	37°(?)
ΔH vap., kcal/mole	4.62	5.6	6.19(?)
Vapour pressure, $\log_{10} p_{mm} =$			
$A − B/T$ (liquid)	A 7.27 B 1030	A 6.53 B 1005	—
$A − B/T$ (solid)	A 8.96 B 1380	A 7.39 B 1220	—
Critical temperature, °C	137°	200°	—
Heat of formation, ΔH_f, 298, kcal/mole[b]	+8(?)	+23.8	—
Bond energy, H—X, kcal/mole[b]	73	64	—
Bond length, H—X, Å	1.46	1.69	—
H—X—H angle[c]	91°0′	89°30′	—
Dissociation constant, HX⁻, K_1	1.30×10^{-4}	2.27×10^{-3}	—
Dissociation constant, X²⁻, K_2	10^{-11}	1.59×10^{-11}	—

[a] Data from ref. 3, p. 43.
[b] S. R. Gunn. J. Phys. Chem. 68 (1964) 949.
[c] $H_2H = 92.1°$.

by magnesium, the volatile product being absorbed in aqueous alkali or silver nitrate solution and followed by its radioactivity. Attempts to prepare it with weighable amounts of the element have been unsuccessful[77].

2.4. CARBONYL COMPOUNDS

Carbonyl selenide and telluride, COSe and COTe, are formed in poor yield by passing carbon monoxide over the elements at 400° (Se[78]) or higher temperatures (Te[79]) and there is some evidence that polonium reacts under these conditions[9]. The selenide is more easily prepared[80] by reaction of aluminium selenide with carbonyl chloride at 219°, and is the best known and most stable of the three compounds; it is a colourless, foul-smelling liquid which boils at −22.9°/725 mm and freezes[78] to a white solid at −122.1°. The vapour pressure is given by

$$\log_{10} p_{mm} = 1149.8/T + 7.4527$$

and the latent heat of vaporization is 5.26 kcal/mole[80].

[75] I. Datta, J. Indian Chem. Soc. 29 (1952) 101, 965.
[76] J. P. Nielsen, S. Maeser and D. S. Jennings, J. Am. Chem. Soc. 61 (1939) 440.
[77] Reference 3, p. 46.
[78] T. G. Pearson and P. L. Robinson, J. Chem. Soc. (1932) 652.
[79] P. L. Robinson and K. R. Stainthorpe, Nature, 153 (1944) 24.
[80] O. Glemser and T. Risler. Z. Naturforsch. 3b (1948) 1.

dinirtogen tetroxide, there being no reaction with the gas, or with gaseous or liquid sulphur dioxide. Tellurium dichloride absorbs dry ammonia gas, possibly forming an amine, but anhydrous liquid ammonia reacts to yield elementary tellurium. A number of complexes are known (p. 1008).

Polonium dichloride[44], a dark ruby-red, hygroscopic solid which sublimes, with decomposition, at 190° in nitrogen, is obtained by reducing the solid tetrachloride with sulphur dioxide (25°), hydrogen sulphide or carbon monoxide (150°) or with hydrogen (200°), but prolonged heating in the last two cases leads to reduction to the element. The compound is also obtained by continued heating of the tetrachloride in a vacuum. Unlike the tellurium compound, it does not disproportionate in water or other solvents, but it is readily oxidized to polonium(IV). Polonium(III) may have a transient existence as an intermediate in this oxidation in hydrochloric acid[90].

Selenium dibromide, like the dichloride, has never been isolated, but it appears to be present in the vapour of the tetrabromide and monobromide, and may be present in equilibrium with the monobromide and tetrabromide in solutions of the latter in carbon tetrachloride[91] or nitrobenzene[92]. Solid tellurium dibromide is known, but it dispro-portionates readily on heating, so that the melting and boiling point cannot be determined. It is a chocolate-brown solid, prepared by vacuum sublimation on to a cold finger of the solid solution of tellurium in tellurium tetrabromide obtained by reaction of the latter with finely divided tellurium in dry ether in the dark or by reaction of bromotrifluoromethane with fused tellurium[93]. Tellurium dibromide disproportionates rapidly in water, liquid sulphur dioxide or hydrogen cyanide, and more slowly in solution in dry ether or chloroform at room temperature, although disproportionation in the last two solvents is rapid on heating. The compound reacts with gaseous or liquid ammonia in the same way as the dichloride; the known complexes are discussed later (p. 1008).

Polonium dibromide[94] is prepared in a similar way to the dichloride, by reduction of the tetrabromide either with hydrogen sulphide at 25° or by heating in a vacuum at 200°, but reduction with sulphur dioxide is incomplete. It is a purple-brown solid which sublimes, with some decomposition, at 110°/30 μ and disproportionates at the melting point, 270–280° in nitrogen; it is reduced to the metal when heated in dry ammonia and is soluble in water and in a number of ketones, the solutions being purple in colour.

The solid diiodides have never been isolated, but selenium diiodide may be present in solutions of selenium and iodine in carbon disulphide[95]; a few complexes of tellurium diiodide are also known (p. 1008).

Tetrafluorides, XF$_4$

Selenium tetrafluoride is a white, hygroscopic solid, melting at −9.5° to a colourless liquid which fumes in air; some physical properties are given in Table 8. It is conveniently made by heating selenium tetrachloride, or, better, selenium with silver fluoride[96], but it is more commonly prepared from the elements[97] at 0°, by the action of fluorine on selenium

[90] K. W. Bagnall and J. H. Freeman, *J. Chem. Soc.* (1956) 2770.
[91] N. W. Tideswell and J. D. McCullough, *J. Am. Chem. Soc.* 78 (1956) 3026.
[92] N. Katsaros and J. W. George, *Chem. Comm.* (1968) 662.
[93] E. E. Aynsley and R. H. Watson, *J. Chem. Soc.* (1955) 2603.
[94] K. W. Bagnall, R. W. M. D'Eye and J. H. Freeman, *J. Chem. Soc.* (1955) 3959.
[95] A. F. Kapustinskii and Yu. M. Golutvin, *J. Gen. Chem.* (*U.S.S.R.*), 17 (1947) 2010.
[96] O. Glemser, F. Meyer and A. Haas, *Naturwiss.* 52 (1965) 130.
[97] E. E. Aynsley, R. D. Peacock and P. L. Robinson, *J. Chem. Soc.* (1952) 1231.

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monochloride[98] or by reaction of sulphur tetrafluoride with selenium dioxide[99] at 100–240°. The compound is then purified by fractional distillation.

The structure[100, 101] of the molecule, obtained by electron diffraction studies is a distorted tetrahedron which results from the replacement of one equatorial bond in a trigonal bipyramid by the lone pair of electrons on the selenium atom, the resulting symmetry[101] being C_{2v}, consistent with the Raman spectrum[102]. Conductivity measurements indicate that there is slight dissociation in the liquid, with the cation being SeF_3^+ and the anion either F^- or SeF_5^-. The known adducts of selenium tetrafluoride (p. 1005) probably involve these ionic species.

Selenium tetrafluoride can be handled in Pyrex when perfectly dry, since it attacks the glass only very slowly. It is a useful fluorinating agent and is completely miscible with diethyl ether, ethanol, iodine pentafluoride and sulphuric acid, and is appreciably soluble in carbon tetrachloride and chloroform. Water hydrolyses it violently and the compound dissolves bromine, iodine, selenium, sulphur and, on heating to 80°, tellurium dioxide but not the trioxide. The tetrafluoride is reduced to selenium by arsine, hydrogen selenide and sulphide, and by potassium iodide, but it reacts with potassium chloride and bromide to form the appropriate selenium tetrahalide.

Tellurium tetrafluoride is also a white, hygroscopic solid, the vapour of which decomposes above 193·8° with the formation of the hexafluoride. It is most simply prepared by reaction of selenium tetrafluoride with tellurium dioxide at 80°, the yield being quantitative[103], and is also formed by the action of nitryl fluoride on tellurium, from the elements at 0° and by the reduction of the hexafluoride with tellurium[104] at 180°.

The crystal symmetry is orthorhombic and the structure in the crystal consists of distorted octahedra linked by *cis* fluorine bridges into endless chains, one apex of each octahedron being occupied by the lone pair of electrons of the selenium atom[105].

Tellurium tetrafluoride is readily hydrolysed and it reacts with glass or silica at 200°. Its chemical behaviour is similar to that of the selenium compound, but it is less useful than the latter as a fluorinating agent.

The involatile product resulting from the radiation decomposition of polonium hexafluoride (p. 964) is probably the tetrafluoride, but the existence of this compound has not been definitely established. A white hydrate (or basic salt) seems to be formed when polonium(IV) hydroxide or the tetrachloride is treated with aqueous hydrofluoric acid[9], but these products have not been investigated.

Tetrachlorides, XCl₄

Selenium, tellurium and polonium tetrachlorides are respectively pale yellow, white and bright yellow, volatile, hygroscopic, readily hydrolysed solids; some physical data are given in Table 8. The selenium compound is almost completely dissociated to lower chlorides and chlorine in the vapour, but the vapour density of the tellurium compound is

[98] P. L. Goggin, *J. Inorg. Nuclear Chem.* **28** (1966) 661.
[99] A. L. Oppegard, W. C. Smith, E. L. Muetterties and V. A. Engelhardt, *J. Am. Chem. Soc.* **82** (1960) 3835.
[100] H. J. M. Bowen, *Nature*, **172** (1953) 171.
[101] V. G. Ewing and L. E. Sutton, *Trans. Faraday Soc.* **59** (1963) 1241.
[102] J. A. Rolfe, L. A. Woodward and D. A. Long, *Trans. Faraday Soc.* **49** (1953) 1388.
[103] R. Campbell and P. L. Robinson, *J. Chem. Soc.* (1956) 785.
[104] J. H. Junkins, H. A. Bernhardt and E. J. Barber, *J. Am. Chem. Soc.* **74** (1952) 5749.
[105] A. J. Edwards and F. I. Hewaidi, *J. Chem. Soc.* (A) (1968) 2977.

normal below 500°, indicating that there is little dissociation in the maroon coloured vapour below this temperature. In contrast, the molten polonium compound, which is straw coloured, becomes scarlet at 350°, probably because of decomposition to the dichloride, and the purple-brown vapour becomes blue-green above 500°, possibly as a result of a progressive decomposition.

The three compounds are commonly prepared from the elements at moderate temperatures or by reaction of the element or its dioxide with chlorinating agents such as carbon tetrachloride, phosphorus pentachloride or thionyl chloride; they are purified by sub-

TABLE 8. PHYSICAL PROPERTIES OF THE TETRAFLUORIDES AND TETRACHLORIDES[a]

	SeF_4	TeF_4	$SeCl_4$	$TeCl_4$	$PoCl_4$
Melting point, °C	−9.5	129.6	305	224	300
ΔH fusion, kcal/mole[b]	—	6.351	21 (?)[b]	4.51	5.2 (?)
Boiling point, °C	106	193.8d	196 sub.	390	390
ΔH vap., kcal/mole[b]	11.24	8.174	21 (?)*	16.83	19 (?)
Vapour pressure (liquid) $\log_{10} p_{mm} = A - B/T$	$A = 9.44$ $B = 2457$	$A = 5.6397$ $B = 1786.4$			
Vapour pressure (solid) $\log_{10} p_{mm} = A - B/T$	—	$A = 9.0934$ $B = 3174.3$	$A = 11.2040$ $B = 3864$		
Heat of formation, $-\Delta H_{f, 298}$, kcal/mole[b]	—	205	46.1	77.4	80 (?)
Free energy of formation, $-\Delta F_{f, 298}$, kcal/mole[b]	—	185	25.9 (?)	57.6	60 (?)
Density, g/cc	2.75 (18°)				

* ΔH sub.

[a] Data from K. W. Bagnall, *The Chemistry of Selenium, Tellurium and Polonium*, Elsevier, Amsterdam, 1966, unless otherwise stated.

[b] A. Glassner, U.S.A.E.C. Report ANL–5750 (1958).

d = decomp.; sub. = sublimes.

limation, usually in an atmosphere of chlorine in order to suppress decomposition. A useful way of preparing the selenium compound consists in reacting chlorine with a solution of the monochloride in ethyl bromide or carbon disulphide, the insoluble tetrachloride precipitating as the reaction proceeds. Residual selenium monochloride is easily removed from the product by washing it with carbon disulphide[81].

Electron diffraction of the vapour of selenium[106] and tellurium[107] tetrachloride indicates that both have a distorted trigonal bipyramidal structure with one of the equatorial positions occupied by the unshared pair of electrons, a structure consistent with the high dipole moment (2.54 Debye) of the tellurium compound[108]. However, in the solid[109–211] and liquid[109] states the infrared and Raman spectra of tellurium tetrachloride indicate that the ions $TeCl_3^+$ and Cl^- are present, in agreement with the observed electrical conductivity of the molten tetrachloride[113]. Infrared and Raman data for solid selenium tetrachloride[109, 110, 112] are interpreted on the same basis, but no information is available for the polonium compound. X-ray crystallographic data are given in Table 9.

[106] R. E. Dodd, L. A. Woodward and H. C. Roberts, *Trans. Faraday Soc.* 52 (1956) 1052.
[107] D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.* 62 (1940) 1267.
[108] C. P. Smyth, A. J. Grossman and S. R. Ginsburg, *J. Am. Chem. Soc.* 62 (1940) 192.
[109] H. Gerding and H. Houtgraaf, *Rec. Trav. chim.* 73 (1954) 737.
[110] N. N. Greenwood, B. P. Straughan and A. E. Wilson, *J. Chem. Soc.* (A) (1966) 1479.
[111] G C. Hayward and P. J. Hendra, *J. Chem. Soc.* (A) (1967) 643.
[112] J. W. George, N. Katsaros and K. J. Wynne, *Inorg. Chem.* 6 (1967) 903.
[113] A. Voigt and W. Biltz, *Z. anorg. Chem.* 133 (1924) 298.

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Selenium and tellurium tetrachlorides are fairly soluble in non-polar organic solvents and the latter, as well as tellurium tetrabromide and tetraiodide, appear to be trimeric in benzene or toluene; in solvents such as acetone and methyl cyanide these compounds behave as 1:1 electrolytes, possibly in the form $(L_2TeX_3)^+X^-$ where L is the solvent[113a]. The selenium compound is also soluble in hot phosphorus(V) oxochloride; there are few data for the polonium compound, which is apparently soluble in ethanol and in thionyl chloride, and slightly soluble in liquid sulphur dioxide. Selenium tetrachloride is a powerful chlorinating agent, converting, for example, tellurium dioxide to the tetrachloride and selenium dioxide to the oxochloride; it is reduced to the monochloride by sulphur or selenium.

All three tetrachlorides react with anhydrous liquid ammonia, the selenium and tellurium compounds forming the nitride (p. 982) and the polonium compound being

TABLE 9. X-RAY CRYSTALLOGRAPHIC DATA FOR THE TETRAHALIDES

Compound	Symmetry and space group	Lattice parameters, Å			Calc. density g/cc	Ref.
		a_0	b_0	c_0		
SeCl$_4$	Monoclinic, C2/c or Cc	16·46	9·73 $\beta = 117°$	14·93	2·63*	a
TeCl$_4$	Monoclinic, C2/c or Cc	16·91	10·36 $\beta = 117°$	15·25	2·95*	a
TeBr$_4$	Monoclinic, C2/c or Cc	17·75	10·89 $\beta = 116°34'$	15·88	4·33*	a
TeI$_4$	Orthorhombic, Pnma-D_{2h}^{16} or Pn2$_1$a-C_{2v}^9 or	15·54	16·73	14·48	5·145*	b
	Tetragonal, I4$_1$/amd-D_{4h}^{19}	16·12	—	11·20	5·7*	b

* 16 molecules/unit cell.

a C. B. Shoemaker and S. C. Abrahams, *Acta Cryst.* 18 (1965) 296.
b W. R. Blackmore, S. C. Abrahams and J. Kalnajs, *Acta Cryst.* 9 (1956) 295.

reduced to the element (p. 946). The tetrachlorides are also reduced to the element by gaseous ammonia, the tellurium compound at 200–250°, the selenium and polonium compounds at room temperature, the last only slowly. Hydrogen sulphide reduces solid selenium, tellurium and polonium tetrachlorides, the first two to the element at room temperature, but tellurium tetrachloride may form the dichloride at low temperature, and the polonium compound forms the dichloride at 150°; the tetrachlorides react with ketones and β-diketones to form organo-compounds (p. 1002). The complexes of the tetrachlorides are discussed later (p. 1007).

Tetrabromides, XBr$_4$

The orange-red selenium, yellow tellurium and bright red polonium compounds are hygroscopic, readily hydrolysed solids which are all rather unstable with respect to decomposition with loss of bromine. Thus selenium tetrabromide decomposes appreciably at room temperature and completely at 70°, giving a mixture of the elements and lower selenium bromides. The tellurium compound decomposes above 280° and it melts, in bromine vapour, at 363°, the boiling point lying between 414° and 427°. However, the vapour density indicates almost complete dissociation to bromine and the dibromide.

[113a] N. N. Greenwood, B. P. Straughan and A. E. Wilson, *J. Chem. Soc.* (A) (1968) 2209.

The polonium compound seems to be somewhat more stable in this respect; it melts in bromine vapour at 330° and boils at 360°/200 mm.

The three tetrabromides are usually prepared from the elements, using an excess of the halogen, the reaction with polonium requiring heating to 200–250° since metallic polonium is inert to gaseous or liquid bromine at room temperature. The selenium compound is also prepared by the reaction of bromine with the monobromide, either alone or in solution in carbon disulphide, chloroform or ethyl bromide and the tellurium compound can be made by reaction of tellurium with iodine monobromide or by dissolving the dioxide in hydrobromic acid and precipitating the tetrabromide from the solution with moderately concentrated (77%) sulphuric acid. The polonium compound is most easily prepared by heating the dioxide in hydrogen bromide or by evaporating to dryness a solution of the dioxide in hydrobromic acid. Tellurium tetrabromide can be purified by sublimation in bromine vapour or by recrystallization from glacial acetic acid.

The infrared and Raman spectra of the solid selenium[112] and tellurium[110–112] tetra-bromides indicate that they are ionic like the tetrachlorides; some crystallographic data are given in Table 9 and the complexes are discussed later (p. 1007).

Selenium tetrabromide is quite soluble in carbon disulphide, carbon tetrachloride, chloroform and ethyl bromide, whereas the tellurium compound is soluble in chloroform and ether, but not in carbon tetrachloride, and polonium tetrabromide is only known to be soluble in ethanol and slightly soluble in liquid bromine. Both the selenium and tellurium compounds react with ammonia to form the nitrides (p. 982), the former in solution in carbon disulphide with the gas and the latter with the anhydrous liquid. Hydrogen sulphide reduces tellurium tetrabromide to the element in solution in chloroform whereas the solid polonium compound is reduced to the dibromide at room temperature.

Tetraiodides, XI_4

Selenium tetraiodide is unknown but anionic iodo-complexes have been isolated; these are discussed later (p. 1006) with the other halo-complexes. The grey-black tellurium and black polonium tetraiodides are appreciably volatile, but decompose on heating, the tellurium compound above 100° and the polonium one above 200°, at which temperature it sublimes in nitrogen, leaving a residue of the metal, possibly because of decomposition to an unidentified lower iodide which subsequently disproportionates. The tellurium compound melts at 280° in a sealed tube, presumably with a considerable degree of de-composition, and two crystal forms are known (Table 9), the orthorhombic one being the more usual. The tetraiodides of the two elements are only slowly hydrolysed by cold water or aqueous alkali, in contrast to the behaviour of the other tetrahalides.

Both tetraiodides are commonly prepared from the elements or by precipitating the compounds from aqueous acid solutions of the quadripositive element, avoiding an excess of hydriodic acid since the compounds redissolve in it to form anionic iodo-complex ions. The tellurium compound is also obtained by heating the element with ethyl iodide or cyanogen iodide and the polonium compound by heating the dioxide in hydrogen iodide at 200°; a black adduct, $PoO_2 \cdot xHI$, is formed in the cold[114]. The far infrared spectrum[110] of tellurium tetraiodide shows that it is ionic, like the tetrachloride.

The two tetraiodides are slightly soluble in acetone and ethanol, but insoluble in dilute mineral acids, aliphatic acids and a variety of non-polar solvents. Tellurium tetraiodide

[114] K. W. Bagnall, R. W. M. D'Eye and J. H. Freeman, *J. Chem. Soc.* (1956) 3385.

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is also slightly soluble in amyl acetate; although the tellurium compound is unaffected by hydrogen at 100° or hydrogen sulphide at 200°, the latter reduces the polonium one to the element at moderate temperature. However, whereas tellurium tetraiodide reacts with dry ammonia at −80°, apparently forming the nitride, the polonium compound does not react with this reagent nor is it reduced in suspension in dilute (0·1 N) hydriodic acid by hydrazine or sulphur dioxide, even at 100°.

Mixed Halides, $XA_nA'_{4-n}$

Dichlorodibromides, XCl_2Br_2, are known for all three elements; the brown-yellow selenium compound appears to be formed by the action of chlorine on an equimolar mixture of selenium monobromide and tetrabromide[115], whereas the yellow tellurium[89] and salmon-pink polonium[94] compounds are obtained by reaction of the dichloride with bromine. The tellurium compound melts to a ruby-red liquid at 292° and boils at 415°. The dichlorodiiodides, XCl_2I_2, are less well established; tellurium dichloride does not react with iodine, but polonium dichloride, when shaken with a solution of iodine in carbon tetrachloride, appears to form a black, unstable chloroiodide[114]. However, the dibromodiiodides, XBr_2I_2, are more stable with respect to disproportionation; the garnet-red tellurium compound is obtained by evaporating to dryness an ethereal solution of tellurium dibromide and iodine. It melts to a dark red liquid at 323–325° and boils, with decomposition, at 420°, the vapour being purple. The black polonium compound[114] appears to be formed when the dibromide is shaken with iodine in carbon tetrachloride, but the dibromide does not react with iodine vapour.

Two other mixed halides are known, yellow-brown selenium trichlorobromide, $SeCl_3Br$, and the yellow-orange chlorotribromide, $SeClBr_3$. The first is precipitated when chlorine is passed into a solution of selenium monobromide in carbon disulphide and the second when the bromine is added to the monochloride in carbon disulphide[115]. The trichlorobromide decomposes appreciably above 208°, but the vapour density is normal, and the chlorotribromide decomposes at about 200°. Raman and infrared spectra[111] of these two compounds indicate that both have an ionic structure as in tellurium tetrachloride. All of the mixed halides are hygroscopic and are readily hydrolysed.

Hexafluorides, XF_6

The hexafluorides are the only hexahalides known; they are gases at room temperature, the selenium and tellurium compounds being colourless in the vapour state, with a rather unpleasant smell reminiscent of the hydrides. Both of the latter condense to white, volatile solids and some physical data are given in Table 10; neither compound attacks glass. The low boiling points of these compounds are noteworthy and are a reflection of the reduced intermolecular attraction resulting from the sheath of non-polarizable fluorine atoms surrounding each chalcogen atom.

Selenium[116], tellurium[117] and polonium[118] hexafluorides are most conveniently prepared from the elements, but other fluorinating agents, such as bromine trifluoride, can be used to fluorinate the dioxide, for example the selenium compound[119]. The compounds are

115 F. P. Evans and W. Ramsay, *J. Chem. Soc.* 45 (1884) 62.
116 D. M. Yost and W. H. Claussen, *J. Am. Chem. Soc.* 55 (1933) 885.
117 R. Campbell and P. L. Robinson, *J. Chem. Soc.* (1956) 3454.
118 B. Weinstock and C. L. Chernick, *J. Am. Chem. Soc.* 82 (1960) 4116.
119 H. J. Emeléus and A. A. Woolf, *J. Chem. Soc.* (1950) 164.